



# Engineered synthesis of hierarchical porous organic polymers for visible light and natural sunlight induced rapid degradation of azo, thiazine and fluorescein based dyes in a unique mechanistic pathway

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## ARTICLE INFO

### Keywords:

Porous organic polymer  
Dye degradation  
Substrate selectivity  
Photocatalysis  
Hierarchical

## ABSTRACT

We report the synthesis of two hierarchical organic polymeric networks for extremely efficient visible light and natural sunlight induced degradation of versatile wastewater organic contaminants under different simulated physical conditions following two distinct mechanistic protocols concomitantly. Tailored synthesis of the polymers by effective utilization of high-dilution-technique leads to extremely low density and hence high dispersibility of the networks featuring impressive surface area and gas adsorption abilities. UV–vis absorption spectra of both composites showed a significant coverage of the natural solar irradiance spectrum. A synthetic control over energy-state potentials allowed the materials to demonstrate an unprecedented dye pollutant degradation capability following two mechanisms, the conventional catalyst sensitized pathway, and a substrate-sensitized secondary pathway, simultaneously. Furthermore, the catalyst exhibited a unique time-dependent, sequential, in-situ alteration in substrate selectivity when subjected to a mixed-component pollutant probe. The photocatalytic ability retained essentially unaltered at outdoor condition under natural sunlight illumination as well as after five successive iterations. This work provides an experimental proof of the concept that strategic synthesis can be employed to control the physical and chemical properties of polymeric networks including their energy-states to achieve novel photo-responsive behaviour, and utilize them as green, sustainable environmentally benign and industrially viable heterogeneous catalysts.

## 1. Introduction

In recent years, semiconducting materials mediated photocatalysis have gained a surging interest for the removal of hazardous toxic substances from the environment through wastewater treatment, indoor air purification etc. in a green sustainable way [1,2]. Despite appreciable progress in the field, most of the materials lack the basic inherent necessities *viz.* an appropriate band-gap with proper valence band (VB) and conduction band (CB) potential configurations, effective exciton separation, and chemical stability [3,4]. Apart from these, a variety of metal oxides and/or other metal complexes that have been widely adopted as semiconductors till date, often suffer from substantial metal leaching, scarcity of natural resources as well as high price, and thereby limiting their utilization in practical purpose [5]. To this end, rationally tailored  $\pi$ -conjugated organic networks (known as

porous organic polymers, POPs) fit well in all the aforementioned criteria and provide suitable semiconducting platforms [6]. POPs are permanently nanoporous three-dimensional materials with relatively high surface area and excellent thermal and chemical stability [7–17]. These structural features make them suitable candidates for highly recyclable heterogeneous catalyst working under even harsh conditions. It has been documented that highly disordered or even amorphous graphitic carbon nitride displays enhanced photoactivity due to effective suppression of the radiative electron-hole recombination [18,19]. Inherent amorphous nature of fully conjugated POPs thus manifests applications in light emission, light harvesting, optical sensing, and photocatalysis in a similar manner [20–26].

A variety of synthetic dyes have been widely used in the textile and printing industries with almost a million ton of annual production [27,90]. Azo dyes (e.g. methyl orange, MO; congo red, CR), thiazin (e.g.

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methylene blue, MB) and fluorescein based dyes (e.g. Rhodamine B, RhB) are the largest class used in the industry and their release in the environment imparts serious ecological damage because of the toxicity, non-biodegradability, potential carcinogenic and mutagenic nature of them [28–31]. Custom designed synthesis of most of these dye molecules possessing chromophore units with high bond energy (e.g. 407 kJ mol<sup>-1</sup> for C=N in RhB, 518 kJ mol<sup>-1</sup> for N=N in MO) [32] make them exceptionally stable, while their ionic structures contribute to high water solubility [33]. Moreover, the presence of these molecules in water significantly decrease the dissolved oxygen level increasing the BOD and COD, which further leads to potential damage of the aquatic life [34,35]. The traditional biological and physical treatment methods such as adsorption, ultrafiltration, coagulation etc. as well as advanced degradation processes of these molecules have met their limitations in some aspects including complex set-up, use of additional additives or peroxides etc. [36–41,90,91]. Therefore, to satisfy the practical need, semiconductor-induced photocatalytic decontamination of wastewater without the use of any additives is emerging as the green alternative.

Sun is the most abundant, clean and safe source of sustainable energy. Approximately  $3 \times 10^{24}$  J energy is delivered from the sun to earth per year, which is almost four times higher than the total annual energy consumption of humans all over the world [42]. Since visible light constitutes more than 45% of total sunlight, whereas hazardous UV light accounts for only 7%, researchers tend to focus on the utilization of visible light energy to carry out versatile transformations [43,44]. Nonetheless, these simulated visible light-induced reactions have enormous environmental advantages, the use of direct sunlight to promote such transformations, which is the ultimate goal for a green sustainable future, is still a long-standing dream [45–48]. In fact, examples of utilizing sunlight for chemical transformations are, to date, extremely rare in literature [49]. Development of a cost-effective and environment-friendly material that can efficiently harvest natural sunlight to promote chemical reactions on an industrial scale, as well as maintain a substantial recyclability is extremely desirable.

Till date, two mutually exclusive mechanistic approaches for the photo-generation of reactive catalytic species have been highlighted to degrade organic dye pollutants: the conventional and straightforward pathway requires the utilization of a semiconductor possessing narrow VB-CB energy gap that can be excited by visible light illumination [50–52], while the other method indulge the use of wide band gap semiconductors furnishing no feasible visible-light-induced activity by its own [42]. In this second method, dye pollutant, adsorbed on the catalytic surface, itself got excited after light illumination and injects that excited electron from their CB to that of the semiconductor to initiate the degradation [53]. Most of the metal based semiconductors and recently benzothiadiazole and polyoxometallate infused POPs have been widely exercised as the first type of materials [54–57], whereas a few surface modified TiO<sub>2</sub> and bismuth based materials are reported to exhibit the second type photoactivity [58–61]. To this end, we envisioned that engineered synthesis of appropriate POP skeletons possessing VB-CB energy gaps in the borderline region compared to the two abovementioned extreme cases should, in principle, bridge these two approaches and impart a unique concomitant photo-activation ability. To examine our proposed concept, we herein report the synthesis of two polymers, one containing no special photoactive unit and another one with azobenzene featuring good surface area and gas adsorption properties and studied the differences in their catalytic ability. Notably, in spite of several literature reports on photoresponsive character of azobenzenes, they have hardly been exercised as potential building units for polymeric semiconducting networks. It has also been documented that degradation of different classes of organic pollutants (cationic and anionic; azo, thiazine, fluorescein etc.) by any single photocatalyst is extremely difficult as they behave differently due to different surface properties [62,63,92,93]. The polymers reported here degraded aqueous solutions of RhB, MB, CR and MO almost quantitatively in a neutral, acidic and alkaline medium using visible light as an

energy source with impressive reaction rate. More importantly, the identical catalytic ability was maintained in outdoor conditions under natural sunlight illumination indicating the sustainable industrial viability of the materials. Most surprisingly, an unprecedented time dependent in-situ alteration in substrate selectivity was observed during degradation of a mixed-dye pollutant probe, which established the feasibility of our proposed concept. To the best of our knowledge, this is the first ever POP-based semiconductor mediated photocatalytic study to address the degradation of a wide variety of environmentally hazardous organic pollutants following a tactically unique mechanistic protocol under visible as well as natural sunlight illumination.

## 2. Experimental section

### 2.1. General methods

Solid state <sup>13</sup>C-CP/MAS NMR spectra analysis were measured on a Bruker Advance 400 DSX spectrometer operating at 100 MHz for <sup>13</sup>C and 400 MHz for <sup>1</sup>H. <sup>1</sup>H-<sup>13</sup>C Cross Polarization Magic Angle Spinning (CP/MAS) were performed at MAS of 10 kHz in a 4 mm zirconia rotor. TPPM decoupling was used for acquisition. The values of chemical shifts are given referenced to TMS. FT-IR spectroscopy was carried out on a Bruker Vertex 80 V FT-IR spectrometer. Powder XRD analyses were performed on a Bruker D8 Advance diffractometer with a copper K $\alpha$  radiation source ( $\lambda = 1.54056 \text{ \AA}$ ) at 40 kV and 45 Ma with 5°/sec scanning speed. The adsorption desorption isotherms were analysed by Micrometrics instrument (ASAP 2020) using ultrapure N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> (99.999%) at 77.3 K. Samples were degassed at 150 °C for 2 h at vacuum prior analysis. Surface area values were calculated using Brunauer-Emmett-Teller (BET) and Langmuir methods at 0.003 < P/P<sub>0</sub> < 0.05 range. Pore size distributions were calculated from N<sub>2</sub> sorption isotherms using the nonlocal density functional theory (NLDFT). Thermal gravimetric analyses (TGA) were carried out on a Netzsch STA 409 thermal analyser under an inert atmosphere at a heating rate of 10 °C/min from room temperature to 1000 °C. The morphology studies were conducted by Scanning Electron Microscopy (SEM) on a JEOL JSM-5610LV (0.5–35 kV) microscope. TEM analysis was carried out using a Philips CM20 microscope at 200 kV. Imaging and diffraction of the structure was performed at low electron dose for minimising beam damage to the sample. The binding energies of the elements present in the polymers were measured by X-ray photoelectron spectroscopy (XPS) on Thermo Fisher ESCALAB 250Xi. UV-vis absorptions of polymers were recorded in solution state on a Shimadzu UV-1800 UV-vis spectrophotometer using a 10 mm path length quartz cuvette at room temperature. 1 mg POPs were dispersed in 3 mL water by ultrasonication prior measurement. Electron paramagnetic resonance (EPR) was measured on Bruker PMX spectrometer at room temperature. Cyclic voltammograms were taken on CHI-660E electrochemical workstation. Total organic carbon (TOC) analyses were performed by a VarioTOC instrument (liquid mode).

### 2.2. Synthesis

Monomer 1,2-bis(3,5-dibromophenyl)diazene was prepared following reported literature procedure [64]. POP-1 and POP-2 were prepared by Sonogashira-Hagihara cross-coupling of 1,4-diethynylbenzene (1.5 eqv.) and corresponding aryl bromides (1 eqv.) in the presence of tetrakis(triphenylphosphine) palladium (0.05 eqv.) and cuprous iodide (0.08 eqv.) in 3:1 mixture of DMF and triethylamine at 80 °C for 72 h under inert atmosphere (Scheme 1). 1,3,5-bromobenzene reacted with 1,4-diethynylbenzene to afford POP-1 network, whereas 1,2-bis(3,5-dibromophenyl)diazene gave POP-2. The solid products obtained after the reaction was repeatedly washed with water and acetone, then treated with methanol and acetone in a Soxhlet for 24 h and dried under vacuum. Both POP-1 (yield 98%) and POP-2 (yield 95%) appeared as yellowish brown powder insoluble in common

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